Potential pollutant sources in a Choptank River (USA) subwatershed and the influence of land use and watershed characteristics

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ABSTRACT

Row-crop and poultry production have been implicated as sources of water pollution along the Choptank River, an estuary and tributary of the Chesapeake Bay. This study examined the effects of land use, subwatershed characteristics, and climatic conditions on the water quality parameters of a subwatershed in the Choptank River watershed. The catchments within the subwatershed were defined using advanced remotely-sensed data and current geographic information system processing techniques. Water and sediment samples were collected in May–October 2009 and April–June 2010 under mostly baseflow conditions and analyzed for select bacteria, nitrate-N, ammonium-N, total arsenic, total phosphorus (TP), orthophosphate (ortho-P), and particle-phase phosphorus (PP); $n = 96$ for all analytes except for arsenic, $n = 136$, and for bacteria, $n = 89$ (aqueous) and 62 (sediment). Detections of *Enterococci* and *Escherichia coli* concentrations were ubiquitous in this subwatershed and showed no correlation to location or land use, however larger bacterial counts were observed shortly after precipitation. Nitrate-N concentrations were not correlated with agricultural lands, which may reflect the small change in percent agriculture and/or the similarity of agronomic practices and crops produced between catchments. Concentration data suggested that ammonia emission and possible deposition to surface waters occurred and that these processes may be influenced by local agronomic practices and climatic conditions. The negative correlation of PP and arsenic concentrations with percent forest was explained by the stronger signal of the head waters and overland flow of particulate phase analytes versus dissolved phase inputs from groundwater. Service roadways at some poultry production facilities were found to redirect runoff from the facilities to neighboring catchment areas, which affected water quality parameters. Results suggest that in this subwatershed, catchments with poultry production facilities are possible sources for arsenic and PP as compared to catchment areas where these facilities were not present.

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1. Introduction

The Chesapeake Bay, the largest estuary in the United States (US), is located in the Mid-Atlantic region, and its 167,000 km^2 watershed is home to 17 million people (US EPA, 2011a). Land use in the watershed is 58% undeveloped and/or forested, 22% agriculture, and 20% developed including 9% urban (US EPA, 2009a). Much of the Chesapeake Bay and its estuaries has been listed by the US Environmental Protection Agency (US EPA) as impaired for sediments and nutrients, both nitrogen and phosphorus (US EPA, 2011a). According to the US EPA Guidance for Federal Land Management in the Chesapeake Bay Watershed (2010), agriculture is responsible for approximately 43% of nitrogen (N), 45% of phosphorus (P), and 60% of the sediment loads released into the Bay. Of this, approximately 17% of N and 19% of P load are due to chemical fertilizer use, and 19% of N and 26% of P load is the result of manure application to cropland (US EPA, 2010). In addition, increased urban runoff and storm water contributions can minimize current agricultural mitigation efforts for N, P, and sediment loads into the Chesapeake Bay (US EPA, 2010). In spite of efforts by the federal government and other non-government organizations to control the amount of pollution entering this important body of water, little success has been observed (US EPA, 2011a). In May 2009, an executive order was issued by US President Obama outlining steps for the restoration and protection of the Chesapeake Bay (Fig. 1) (Executive Order 13508: Chesapeake Bay protection and restoration, 2009) emphasizing the use of adaptive management for

the implementation of current data in decision-making, identifying measurable indicators for evaluating environmental conditions, and coordinating programs and strategies among federal agencies for greater effectiveness.

The Choptank River is an eastern-shore tributary of the Chesapeake Bay; its watershed is an estuarine tidal embayment spanning 2057 km^2 (Fig. 1). Parts of the Choptank River have been classified as "impaired waters" under the Federal Clean Water Act (Maryland Department of the Environment, 2004) due to fecal coliform, nutrients, and sediments. The estuary has received low scores on the biotic integrity surveys conducted and has exhibited a decline of submerged aquatic vegetation (Maryland Department of Natural Resources, 2008). Approximately 60% of its land use is devoted to agriculture: corn (*Zea mays* L.), soybean (*Glycine max* L.), wheat (*Triticum aestivum* L.), and barley (*Hordeum vulgare* L.) (Fisher et al., 2006). Most of these crops are grown to support small- and medium-sized animal feeding operations (AFOs) within the watershed, which are primarily poultry production facilities with some dairy and horse husbandry.

Nearly 560 million broilers were produced on the Delmarva Peninsula in 2010 (Delmarva Poultry Industry, Inc., 2010). A typical producer will grow 5.5 flocks in one or more houses; each house is 15.2 to 20.1 m wide and up to 183 m long and contains 20,000–50,000 birds. Chicks mature approximately six weeks after placement in the house; harvest is followed by a 1 to 2 week period where the poultry house remains empty (University of Maryland Cooperative Extension, 2009). Manure removed from poultry houses is stored and is routinely used as fertilizer on agricultural fields in the spring. Land application of poultry litter is closely supervised, as submission of nutrient management plans is required to help ensure that overload or leaching of nutrients is minimized (Maryland Department of Agriculture, 2010). Weather conditions are also closely observed because application of these materials cannot occur if storms or other harsh weather are imminent. Buffer zones and riparian areas are mandated and encouraged to protect nearby surface and sub-surface water (Maryland Department of the Environment, 2010). Potential pollutants from agriculture and animal product and husbandry include nutrients, arsenic, and non-indigenous microorganisms.
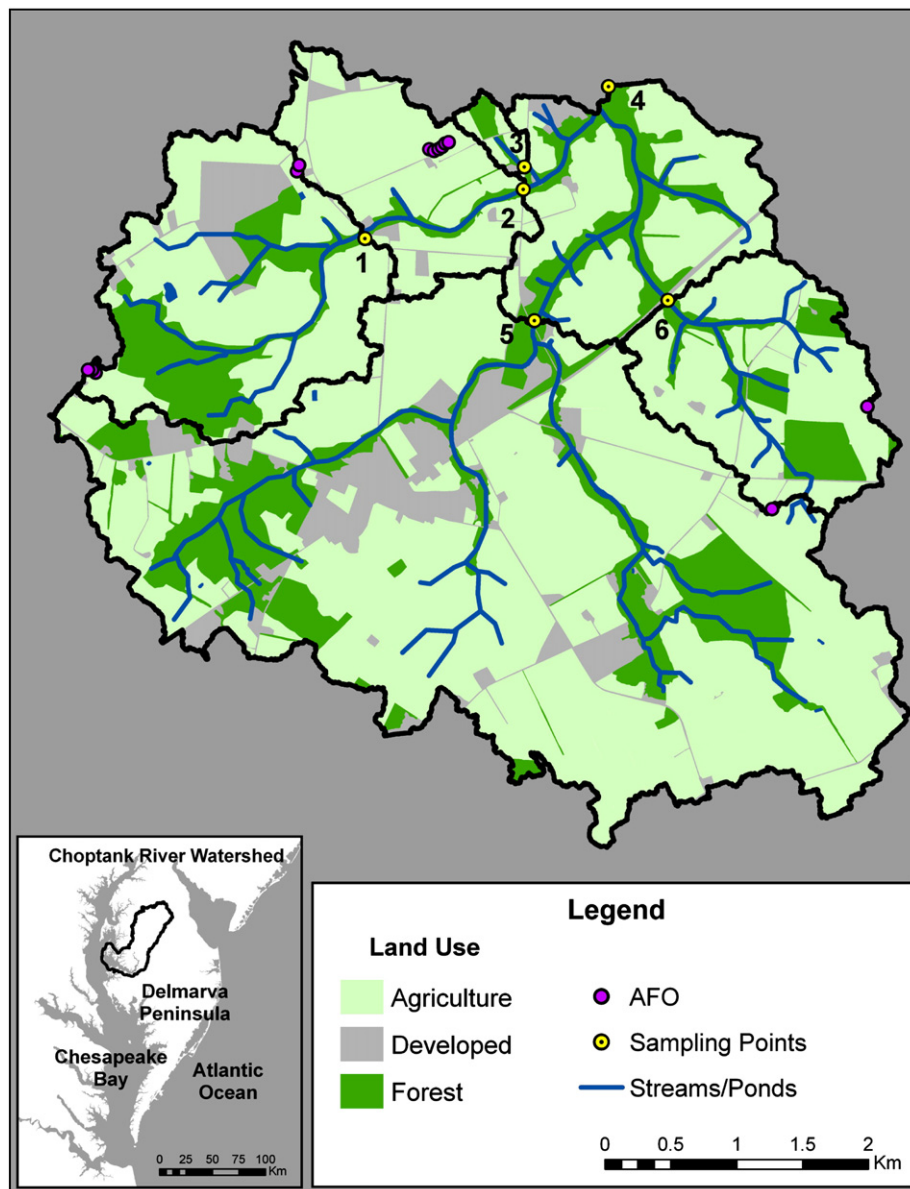
Fig. 1. Subwatershed in the Choptank River watershed with stream catchments with land use, sampling sites, and poultry houses indicated. Catchments 1, 3, and 6 receive runoff from poultry production facilities directly. Catchment 2 also includes catchment 1 and site 4 is the outlet of the entire subwatershed.

Though nitrogen and phosphorus are essential nutrients that regulate many cell functions, an over-abundance of the these nutrients in the water column due to leaching and/or runoff can cause population booms of aquatic plants and other autotrophs (eutrophication), which can lead to other problems such as hypoxia and subsequent fish kills. At present, no formal environmental water quality criteria exist for nitrogen and phosphorus, although statistical analysis of national water quality data has suggested that appropriate reference levels for nitrogen range from 0.12 to 2.2 mg/L and for phosphorus below 0.1 mg/L, which is often the limiting nutrient for algal growth (US EPA, 2008). The reference level for phosphorus, however, may be too high since nuisance algal growths can occur in water bodies that meet this criterion; a more appropriate criterion may be 0.01 to 0.075 mg/L (US EPA, 2008). The drinking water maximum contaminant level (MCL) for nitrate is 10 mg/L (US EPA, 2009b, 2009c).

According to the US EPA (2009d), the most common contributors of excess nitrogen and phosphorus are fertilizers used on commercial and residential lands, runoff from croplands, AFOs, wastewater treatment plant discharge, and overflow/leaks from septic systems. Phosphorus and nitrogen follow different transport pathways; phosphorus tends to move with surface runoff, whereas nitrogen travels downward through soil and then moves out with groundwater (Logan et al., 1994; Vervoort et al., 1998; Erickson et al., 2001). A study done by Chaubey et al. (2007) in northwestern Arkansas (USA) found that during the winter and spring months, sediment appeared to be releasing dissolved inorganic P, whereas during the summer and fall, sediment acted as a sink. Ultimately, they concluded that the stream's ability to assimilate nutrients was the deciding factor in the magnitude and behavior of transported nutrients (Chaubey et al., 2007).

Metalloids and metals such as arsenic, copper, lead, and zinc are naturally occurring minerals that can be found almost anywhere; their presence in soil and water does not always indicate anthropogenic activity. The greatest concentration of metals and metalloids would be expected in soil and stream sediment because they can readily complex with organic matter and with clay particles (Gupta and Karuppiah, 1996; Lin and Puls, 2000). The US Geological Survey (USGS) May 2000 county map shows that on Maryland's eastern shore approximately 25% of groundwater samples (average depth of 35 m) contained arsenic concentrations greater than $1 \, \mu g \, L^{-1}$ (USGS, 2009). Soil arsenic concentrations in this area are typically less than $0.5 \, mg \, kg^{-1}$ (Codling et al., 2008).

The US freshwater acute exposure (criterion maximum concentration) and chronic exposure (criterion continuous concentration) levels for arsenic are $340 \, \mu g \, L^{-1}$ and $150 \, \mu g \, L^{-1}$, respectively (US EPA, 2009c), whereas the US EPA MCL for arsenic is 10 μg/L (US EPA, 2009b). The largest non-natural sources of arsenic, both current and historic, include livestock feed additives such as roxarsone; lead arsenate, a legacy pesticide used to control the codling moth in apple orchards; arsenic trioxide, a smelting byproduct; chromated copper arsenate from pressure-treated wood, and the burning of fossil fuels especially in urban areas (Murphy and Aucott, 1998; Smedley and Kinniburgh, 2002; Balasoiu et al., 2001). Smelting and production of pressure treated wood are not found in this area. With the application of poultry manure for the crop growing season, the use of arsenical feed additives for poultry, and the large precipitation events typical of spring, an arsenic pulse might be expected in surface water in the spring.

Surface runoff is the major transport process that carries sediment and anything sediment-associated, like chemicals or microbes, off the land and into nearby surface water. Pathogenic bacteria are almost always present in surface waters (Ford, 1999). It is the number in which they exist, the presence of antibiotic-resistant strains, and whether or not they are native species that makes their presence a concern. In dealing with AFOs, concerns center not only on release of pathogens from litter/manure into surface or groundwater, but

also on zoonoses, the ability of a disease to transfer from animal to human (Gilchrist et al., 2007). The direct enumeration of pathogenic species is complex, expensive, and time consuming, making this accurate and direct approach unrealistic.

Traditional proxy measurements, including particle counting and turbidity, look at related and easy to assess indicator organisms (Brookes et al., 2004). Total and/or fecal coliforms, fecal streptococci, and *Enterococci* are the indicators commonly used (Brookes et al., 2004; Kashefipour et al., 2006), though there is argument that these species are not indicators of potential health risks. Fecal coliforms and *Enterococci* are the indicator organisms used by wastewater treatment facilities to judge water quality, thus this convention may be hard to change, especially if detection of other (better) indicators is time consuming and costly.

Examples of alternative and conservative water quality indicator species include *Cryptosporidium parvum* a long-lived species with highly resistant oocysts, and *Clostridium perfringens* whose spores are resistant to predation and appear in sediment (Brookes et al., 2004). However, widespread adoption is hindered by their anaerobic needs and the difficulty of cultivating their vegetative forms. Other species related to poultry AFOs are the *Bacteroides* group (Haack et al., 2009), *Bifidobacterium* spp., *Lactobacillus* group, *Veillonella* spp., *Atopobium* spp., and *Campylobacter* spp. (Wise and Siragusa, 2007) all of which are anaerobic opportunists.

A number of long-term ecological and air and water quality studies have been carried out in the Choptank River watershed by the Maryland Department of Natural Resources, US EPA Chesapeake Bay Water Quality Monitoring Network, United States Department of Agriculture-Agricultural Research Service (USDA-ARS), USGS, the University of Maryland Horn Point Laboratory, and the National Oceanic and Atmospheric Administration-National Centers for Coastal Ocean Science (Whitall et al., 2010 and references therein). The Choptank River watershed has also been included in Conservation Effects Assessment Project (CEAP), a national study to discern and quantify agricultural best management practices (McCarty et al., 2008). However, none of these studies to date has combined measurements of nutrients, arsenic, and microorganism with a detailed examination of land use to elucidate potential ecosystem land use indicators.

The survey described in this paper was conducted to explore, at greater spatial resolution, the connections between certain uses of land and water quality of adjacent bodies of surface water. A broad spectrum of sampling parameters was coupled with detailed land use data and remotely-sensed data to explain trends in analyte observations. This paper highlights pollutant tendencies and the importance of topographic and hydrologic characteristics and climatic conditions. A better understanding of these features and local natural attenuation predispositions will support mitigation practices already in place for the protection of surface waters and will contribute to the goals of CEAP.

2. Materials and methods

2.1. Sampling site description

The Choptank River watershed is a site of focused long-term environmental research associated with the USDA Conservation Effects Assessment Project (Hively et al., 2011; McCarty et al., 2008; USDA-NRCS-CEAP, 2010; Whitall et al., 2010). One subwatershed within the Choptank River watershed was chosen as the study site. The Choptank River watershed is located on Mid-Atlantic Coastal Plain soils (Ator et al., 2005) with parent materials defined by superposition of upper-delta-plain sands and gravel on marine-inner-shelf sands and a surficial unconfined aquifer ranging in depth from 8 to more than 30 m (Phillips et al., 1993). The subwatershed soil type includes the Mattapex series (fine-silty, mixed, active, mesic aquic

hapludults) which are moderately well drained with moderate or moderately-low permeability (Soil Survey Staff, 2010). Sampling sites were established at the outlet (site 4) of the subwatershed and at 5 upstream sites that were accessible from public areas to avoid biosecurity concerns at the commercial poultry production facilities (Fig. 1).

2.2. Sample collection

Sample collection occurred on an approximately biweekly basis at six sites in a subwatershed in the Choptank River watershed from May to October 2009 and April to June 2010; nutrients, arsenic, and bacteria samples were collected on 10, 12, and 11 dates, respectively (Fig. 1). All sampling was carried out at least two days (except for June 10, 2009) after any large rainfall–runoff event occurred (greater than 10 mm). Streambeds shifted and depth varied somewhat during the sampling period. Stream flows also varied and ranged from no flow to less than 5 m^3/s as was observed at the closest USGS monitoring station (USGS 01491500: 38.96681, −75.94606) which is located in the Choptank River watershed and is within 15 km of the study subwatershed (Fig. 2). Baseflow was confirmed at the USGS site using hydrograph separation with a recursive digital filter for perennial streams with porous aquifers, with a filter parameter of 0.98 and a maximum baseflow index value (BFI$_{max}$) of 0.80 (Lim et al., 2005). June 10, 2009 samples were collected one day after a 27 mm rain event; flow was 39% above baseflow on the recessional limb of the hydrograph. Precipitation data records were obtained from the National Oceanic and Atmospheric Administration (NOAA) database for the Royal Oak, MD station which is located just outside the Choptank River watershed (Index No. 7806) (NOAA, 2011) and approximately 30 km from the subwatershed. Observations at private rain gauges located near the subwatershed sampling points were similar to data collected at the NOAA station, therefore, only NOAA data are presented here.

Water temperature and conductivity were measured at the midpoint between the water surface and the bottom of the stream using an YSI 556 multi-parameter field meter (Geotech Environmental Equipment, Inc., Denver, CO) (Table 1). Water samples were collected to test for arsenic, bacteria, and nutrients from the center of stream flow with a stainless steel pail. For arsenic analysis, samples were poured into acid-washed, 150-mL HDPE Nalgene plastic bottles, each containing 1 mL of 1 N nitric acid, and kept at ambient

Table 1
Mean ± standard deviation of water quality parameters for each catchment.

Catchment	pH	Conductivity (mS/cm)	Total dissolved solids (g/L)	Dissolved oxygen (mg/L)	Temperature (°C)
1	6.5 ± 0.6	0.3 ± 0.06	0.2 ± 0.04	6.6 ± 3	16.2 ± 3.0
2	6.6 ± 0.6	0.3 ± 0.04	0.2 ± 0.03	7.2 ± 4.5	15.8 ± 2.5
3	6.5 ± 0.7	0.3 ± 0.08	0.2 ± 0.06	7.1 ± 3.0	16.3 ± 4.2
4	6.8 ± 0.6	0.4 ± 0.1	0.3 ± 0.09	6.6 ± 4.2	16.6 ± 2.8
5	6.7 ± 0.5	0.5 ± 0.1	0.4 ± 0.1	7.8 ± 3.1	17.4 ± 2.2
6	6.9 ± 0.6	0.3 ± 0.05	0.2 ± 0.02	7.6 ± 3.4	16.8 ± 3.6

temperature until analyzed, usually within 1 week of collection. For bacteria counts, samples were stored in 500-mL, amber bottles that had been washed with detergent, distilled water rinsed, methanol rinsed, and baked for 4 h at 400 °C. For nutrient analysis, samples were stored in clear, acid-washed 250-mL, glass bottles. Nutrient and bacterial samples were kept on ice in the field, transported to the laboratory, and stored at 4 °C; processing took place within 24–48 h after collection.

Sediment samples were collected using wide-mouthed, 150-mL, sterilized and sealed, amber jars. The top 4–6 cm of stream bed was collected at either the middle of the stream or from the depositional zone (area along the shore edges where sediment typically deposits) using the jar itself as the sampling device. Care was taken to collect the easily-disturbed top layer along with the water directly above the sediment. Samples were stored at 4 °C and processed within 24–48 h after collection.

2.3. Sample analysis — nutrients and arsenic

Nutrient samples were divided to accommodate analyte requirements. Dissolved nitrate-N (NO_3^-/NO_2^-), ammonium-N (NH_4^+), and dissolved reactive P (ortho-P) were measured from a filtered (sterile Pall GN-6 Grid filter membrane, mixed cellulose esters, pore size = 0.45 μm) sample portion; total phosphorus (TP) was measured from an unfiltered sample digested portion (persulfate digestion; Pote and Daniel, 2000). Nutrients were measured using a Lachat QuikChem 8000 flow injection analyzer (Lachat Instruments, Milwaukee, WI) (Pote and Daniel, 2000). Total arsenic concentrations were determined using the hydride method with inductively coupled plasma optical emission spectrometer (Optima 4300 ICP-OES, Bradford,
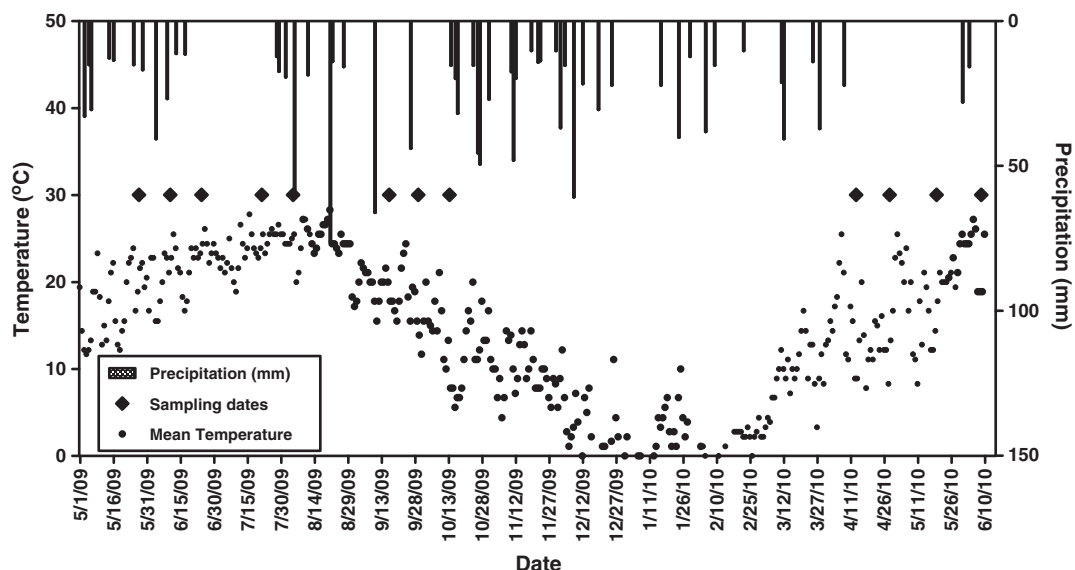
Fig. 2. Precipitation, temperature, and sampling dates for the subwatershed in the Choptank River watershed.

CT), according to the method outlined by Anderson and Isaacs (1995) and Arikan et al. (2008). Limits of quantitation (LOQs) are listed in Table 2.

2.4. Sample analysis — bacteria

Water samples were shaken to re-suspend all bacteria and particles that may have settled during storage. Appropriate sample volumes were added to IDEXX 100-mL sample bottles, according to detection limits of Colilert-18 and Enterolert test kits (IDEXX Laboratories, Inc.). Two dilutions were made using sterile de-ionized (DI) water. Each dilution was treated as a replicate and separate sets were prepared for each group of interest (*Enterococcus* or *Escherichia coli*). Samples were prepared, incubated, and quantified following IDEXX kit directions (IDEXX Quanti-Tray/2000, IDEXX Laboratories, Inc.).

Sediment samples were prepared according to modified standard methods (Camper et al., 1985; US Food and Drug Administration, 2002; Garzio-Hadzick et al., 2010). Ten grams of well-mixed sediment were blended on high speed for 2 min with 100 mL of sterilized DI water, and then poured into a 250-mL beaker and allowed to settle for approximately 1 h. A measured amount of supernatant (0.5–10 mL) was added to a 100-mL IDEXX bottle according to detection limits of Colilert-18 and Enterolert test kits (IDEXX Quanti-Tray/2000, IDEXX Laboratories, Inc.) and diluted with sterile DI water. Each of the two dilutions was treated as a replicate and separate sets were made for each group of interest (*Enterococci* or *E. coli*). Samples were prepared, incubated, and quantified following IDEXX kit directions. All trays were sealed using an IDEXX Quanti-Tray sealer. Limits of quantitation (LOQs) are listed in Table 2.

2.5. Subwatershed delineation

The subwatershed in the Choptank and its contributing areas for the six sampling points were derived from a Light Detection and Ranging (LiDAR) 1 m resolution digital elevation model (DEM) data using the Hydrology Toolkit in ArcMap 9.3.1 (Esri, Redlands, CA) and converted to vector shapefiles.

2.6. Land use data development

The boundaries of the study area were delineated using a 1-m resolution bare earth LiDAR DEM. The LiDAR data were collected for the Maryland Department of Natural Resources (MD DNR) during spring 2003 and spring 2006. These datasets had a vertical accuracy of less than or equal to 18 cm RMSE and were designed to meet or exceed the Federal Geographic Data Committee national standard for spatial data accuracy guidelines for data at 1:2400. Estimated horizontal positional accuracy of point returns exceeded 0.5 m.

A stream map was created using a combination of automated processes within ArcMap 9.3.1 and hand editing. First, impediments

to two-dimensional flow were identified and removed using LP360 software (QCoherent, Colorado Springs, CO) to lower MD DNR bare earth LiDAR point elevations to the level of flowing water. After rasterization to 1 m, ArcMap 9.3.1 was used to delineate stream networks automatically at flow accumulation thresholds of 300,000 pixels or 30 ha. Additional perennial and intermittent channels were then added by hand to the 300,000 threshold product using the procedure described in Lang et al. (2012). The resultant product was considerably more accurate than the most detailed nationally available stream datasets (i.e., High Resolution National Hydrography Dataset; Lang et al., 2012). The land use listed in Table 3 was categorized as previously described (Hively et al., 2011). Developed areas included industrial, residential, farm buildings, other miscellaneous buildings, and roads. Poultry houses were the only AFOs in this subwatershed.

2.7. Statistical analysis

GraphPad Prism® 5 (GraphPad Software, Inc., La Jolla, CA) or Microsoft® Excel 2007 software (http://office.microsoft.com) were used for all statistical calculations. Statistically significant relationships had error probabilities (p) less than 0.05. Means and medians were calculated using individual, un-weighted values for each sample within a group. To test for differences between sampling sets, a one-way analysis of variance (ANOVA) was done using a Kruskal–Wallis test (non-parametric, non-Gaussian distribution) followed by a Dunn's post test. Box-plot analyses were used to assess temporal and spatial variability in analyte concentrations. Spearman ranking correlation was used to assess the relationship between analytes contained in each sample. Single variable linear regression was used to assess the relationship between the mean observed analyte concentrations and subwatershed land use parameters; R^2 values reported reflect the accuracy of the regression line to describe the data.

3. Results and discussion

3.1. Land use and characteristics

The number of poultry houses and land use classification determined for each catchment area are shown in Table 3. Poultry houses were identified based on size, layout, and support building and equipment proximity; the count reflects their physical location within each catchment area. Poultry houses that were on boundary lines were assigned to the catchment containing the majority of the facility. Although drainage from some of the poultry houses was contained in the catchment area where the houses were physically located, in two cases, the runoff from these houses was redirected by flow impediments (i.e., roadways) to another catchment area. This was ascertained by analyzing impervious surface placement, surface water location and flow characteristics, and topographic information using LiDAR and aerial photography data. Catchment area 2 contained the most poultry houses, six at one location plus five contained in catchment area 1, which drained into catchment area 2. However, runoff from the six

Table 2
Summary of samples collected with concentrations and limit of quantitation (LOQ).

Analyte	Number (n)	Units	Minimum	Maximum	Median	Mean ± SD	LOQ
E. coli (aqueous)	89	MPN/100 mL	20	10,500	504	877 ± 1260	1
Enterococci (aqueous)	89	MPN/100 mL	10	14,100	511	1020 ± 1720	1
E. coli (sediment)	62	MPN/10 g$_{ww}$	84	24,300	1701	3690 ± 5720	1
Enterococci (sediment)	62	MPN/10 g$_{ww}$	85	25,000	691	4140 ± 6290	1
Arsenic	136	μg/L	0.090	4.0	0.41	0.58 ± 0.60	0.14
Nitrate-N	96	mg/L	0.037	12	5.7	5.8 ± 3.5	0.01
Ammonium-N	96	mg/L	0.034	2.7	0.35	0.54 ± 0.63	0.01
Total P	96	mg/L	0.026	0.47	0.089	0.13 ± 0.10	0.01
Ortho-P	96	mg/L	0.026	0.30	0.052	0.076 ± 0.064	0.01
Particulate P (PP)	96	mg/L	0.003	0.41	0.037	0.063 ± 0.088	–

Table 3
Land use totals in hectares (ha) and percentage of total area for the subwatershed of the Choptank River watershed. The developed land use category is delineated; farmyard does not include AFOs.

Catchment	Total area	Agriculture		Poultry houses	Forest		Developed	
	(ha)	(ha)	(%)	(count)	(ha)	(%)	(ha)	(%)
1	370	214	58	5	103	28	49	13
2 (includes 1)	571	382	67	11	116	20	64	11
3	18	10	54	–	7	39	1	7
4 (outlet)	2614	1772	68	13	547	21	279	11
5	1477	1000	68	1	280	19	191	13
6	260	192	74	1	61	23	6	2

Catchment	Developed									
	Industry		Residential		Road		Building		Farmyard	
	(ha)	(%)	(ha)	(%)	(ha)	(%)	(ha)	(%)	(ha)	(%)
1	–	–	42	11	4	1	–	–	4	1
2 (includes 1)	–	–	52	9	9	2	–	–	4	1
3	–	–	1	4	0	3	–	–	–	–
4 (outlet)	21	1	182	7	38	1	9	0	29	1
5	21	1	117	8	21	1	9	1	23	2
6	1	0	2	1	3	1	–	–	1	0

houses clustered together drained to catchment area 3 along a roadway not into catchment 2 (Fig. 1). Similarly, runoff from the one house in catchment area 5 was redirected to catchment area 6. In areas of low topographic relief, like the study area, watershed boundaries are difficult to delineate accurately with automated methods because anthropogenic features can easily redirect surface flow.

3.2. Nutrients

Total phosphorus (TP) and orthophosphate (ortho-P) concentrations were measured, and the particulate organic and inorganic P fraction, referred to as the particulate P (PP), was calculated as the difference of ortho-P from TP (Fig. 3). Ortho-P is utilized by aquatic plants and animals, whereas animals can also consume PP (US EPA, 1997). The mean concentrations for TP, ortho-P, and PP were 0.13 ± 0.1 mg L^{-1}, 0.076 ± 0.064 mg L^{-1}, and 0.063 ± 0.088 mg L^{-1}, respectively. These concentrations fall within the lower range (less than 0.1 mg L^{-1}) of concentrations for ortho-P as defined in the US EPA Report on the Environment (2008).

Ortho-P contributions to the Choptank River watershed have been documented (Fisher et al., 2006; Sprague et al., 2000; Staver et al., 1996; Whitall et al., 2010). Non-agricultural ortho-P sources include septic systems from residential areas and wastewater treatment plants. In the current study, the largest average concentration of ortho-P (0.13 mg L^{-1}) for any catchment was observed at site 5, which also has the largest amount of residential area and received no direct runoff from poultry production facilities. The largest average concentrations of PP were found at sites 1 and 3, followed by site 6. These three catchments (1, 3, and 6) received runoff from poultry production facilities.

A temporal comparison of the median concentrations of ortho-P and PP (Fig. 4A, B) showed no significant differences, which is consistent with previous work (Hively et al., 2011). The largest concentration values for ortho-P were observed at sites 4 and 5 on September 29 and October 14, 2009, while the largest concentration values for PP were at site 3 on September 19, 2009 and site 1 on April 13, 2010. These observations further indicate that residential areas are a source for ortho-P and poultry production facilities are a source for PP.

Nitrate-N (NO_3^-/NO_2^-) and ammonium-N (NH_4^+) concentrations were measured at all sites, and in all catchments, the predominant form was nitrate-N (Fig. 3B). The average concentrations for nitrate-N and ammonium-N were 5.8 ± 3.5 mg L^{-1} and 0.54 ± 0.63 mg L^{-1},

respectively. The distribution of nitrate-N concentrations observed in this study were comparable to the concentrations observed in 130 agricultural streams across the US (US EPA, 2008). Sixteen percent of all nitrate-N concentration values were less than 1 mg L^{-1}, 41% were greater than 1 mg L^{-1} but less than 6 mg L^{-1}, 31% were greater than 6 mg L^{-1} but less than 10 mg L^{-1}, and 12% of samples exceeded 10 mg L^{-1}.

Larger mean concentrations of nitrate-N were observed at sites 2, 4, and 5, and these catchments also had smaller mean concentration values for PP. Conversely, the smaller mean concentrations for nitrate-N and larger mean concentrations of PP were observed at
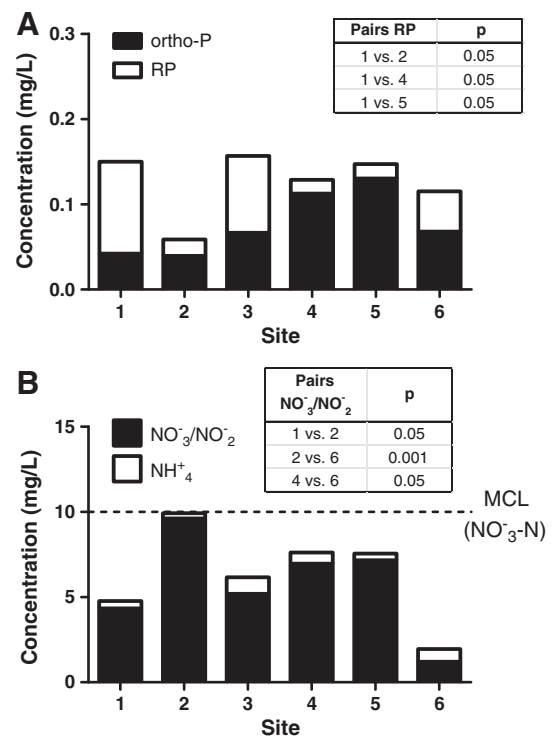
Fig. 3. Spatial analysis of average concentrations of nutrients: A — ortho-P and remaining P (PP) and B — nitrate-N and ammonium-N. Significant differences in the median concentrations for paired sites are listed.
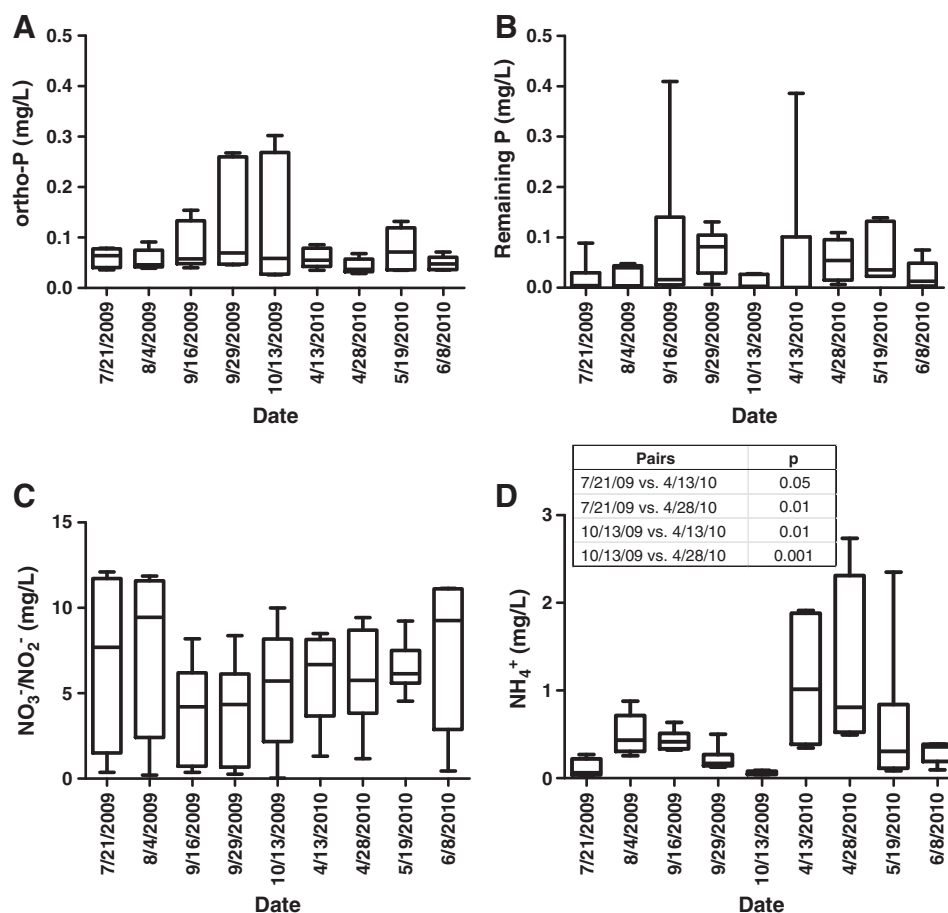
Fig. 4. Temporal analysis of nutrients: A — ortho-P, B — remaining P (PP), C — nitrate-N, and D — ammonium-N. Whiskers represent minimum and maximum values, the box encloses the interquartile range, and the line within the box represents the median. Significant differences in the median concentrations for paired sampling dates are listed.

sites 1, 3, and 6. The relationship between nitrate-N and PP concentration values for each sampling date was examined at each catchment and no significant correlation was observed at any of the sites. This is consistent with the different transport processes for nitrogen and phosphorus observed in this region where nitrate-N is dependent on groundwater delivery to streams (Staver and Brinsfield, 1998; Böhlke and Denver, 1995) and overland flow is the primary transport process for phosphorus (Kleinman et al., 2009). In addition, for each sampling date, nitrate-N concentrations were 1.8 to 2.6 times greater at site 2 than site 1, which receives the runoff from houses located at the far edge of catchment 2 and drains into catchment 2. This indicates an additional source of nitrate-N in catchment 2 that exceeds any nutrient utilization in the stream. Temporal evaluation of the median nitrate-N concentrations (Fig. 4C) showed no significant differences as was observed previously (Hively et al., 2011). However, slightly higher median concentrations were observed during drier months (late July–early August 2009, and April–May 2010), reemphasizing that nitrate-N delivery to streams is primarily via groundwater and not overland flow.

Ammonium-N concentrations were much lower from July to October 2009 than those observed in the April 2010 (Fig. 4D). This pattern is expected because more ammonia is emitted to the atmosphere in late March and April due to application of manure to the surrounding fields. Although ammonia volatilization increases with temperature, it decreases with increasing relative humidity (Huijsmans et al., 2001). Late summer and the fall of 2009 were much wetter compared to the April–May 2010 when little precipitation occurred and temperatures were somewhat higher than normal, (Fig. 2). The lower moisture of April and May 2010 facilitates higher
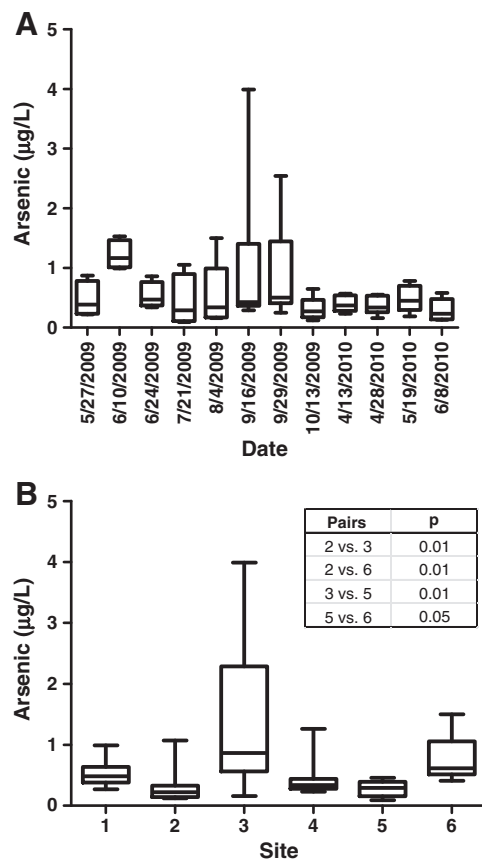
ammonia emissions and presumably greater deposition to streams. On three sampling dates in spring 2010, five samples contained much higher values of ammonium-N than all the other samples: sites 3 and 6 on April 13, sites 3 and 4 on April 28, and site 6 on May 19, 2010. Surprisingly, the highest ammonium-N concentration value was observed at site 4 which receives waters from all the subwatershed catchments and should be more dilute. Therefore, another process other than stream transport, such as atmospheric emission and deposition, must be involved.

Atmospheric ammonium-N concentrations in samples collected at the nearby Blackwater National Wildlife Refuge, a Clean Air Status and Trends Network (CASTNET) site, were examined to discern if ammonium-N concentrations were larger in the spring (US EPA, 2011b). No temporal trend was found; however, these ammonium-N data (obtained from two-week composite samples) may not reveal the exceptionally high, local ammonia-N emissions that can occur on manure or fertilizer application days because the sampling resolution was insufficient to detect these changes. Thus, the larger values of ammonium-N observed in spring water samples may be due to deposition of ammonia emitted from local sources (Asman et al., 1998). The influence of wind direction and wind speed would be minimal in this area because manure is applied to many fields all around the same time. By June, no high values are observed which is consistent with little or no additional fertilizer and manure application beyond late May in this region. In addition, lower nitrification rates due to lower springtime water temperatures (mean water temperature for April and May = 13.1 °C ± 1.2 °C) may also contribute to the higher ammonium-N values observed in the spring (Zhu and Chen, 2002).

3.3. Arsenic

The average concentration of total arsenic for all samples in this study was $0.59 \pm 0.6~\mu g~L^{-1}$ and ranged from 0.0 to $4.0~\mu g~L^{-1}$, which is well below the MCL for drinking water (US EPA, 2009b). Although no significant differences in the median arsenic concentrations were observed between sampling dates, the arsenic concentrations measured on June 10, 2009 at each catchment site were consistently higher compared to the values on the other sampling dates (Fig. 5A). Flow on this date was 39% above baseflow on the recessional limb of the hydrograph as was calculated using the procedure described by Lim et al. (2005). This is not unexpected as arsenic is readily removed from soils with water, and overland flow from rain events can cause an increase in the amount of arsenic delivered to streams especially after manure is applied in the spring (Rutherford et al., 2003). The highest arsenic concentration values were observed in late summer 2009 at sites 3 and 6 following large precipitation events (greater than 35 mm). Both catchment 3 and catchment 6 receive runoff from poultry production facilities. Furthermore, the median concentration values at these sites were significantly greater ($p<0.05$) than the median concentration values calculated for catchments 2 and 5 which do not receive direct runoff from poultry production (Fig. 5B).

At environmentally-relevant pH values, arsenic sorbed on soil surfaces can be readily displaced by ortho-P (Codling, 2007; Codling et al., 2008; Thanabalasingam and Pickering, 1986; Peryea, 1991). However, in examining the entire data set of this study and each catchment separately, essentially no Spearman ranking correlation was observed between arsenic and ortho-P concentrations. In a recent study, arsenic and phosphorus concentrations were examined in

ditch waters draining point (poultry barnyards) and non-point sources (fields where poultry litter was applied), and arsenic and phosphorus in the water were correlated only in ditches draining point sources (Church et al., 2010). The relationship between mean PP concentration and mean arsenic concentration for each site in the current study was also considered, and a moderate positive correlation was found ($R^2 = 0.64$, $p = 0.06$). This suggests that the transport mechanism of arsenic and PP are similar.

3.4. Bacteria

Enterococci and *E. coli* were measured in water samples and in the sediment at each site (Table 1). The largest bacterial counts in the water column were observed on June 10, 2009 (higher flow) and were significantly greater ($p<0.05$) than the smallest bacterial counts in the water column, which were observed on the driest sampling days in April 2010 (Fig. 6A, B). Increases in bacterial counts as a function of flow have been observed and have been attributed to overland flow inputs and/or disruption of the bacteria in the sediment beds (e.g., Hunter et al., 1992). Site profiles of these two groups of organisms remained relatively steady throughout the sampling regime and no significant differences between sites were observed
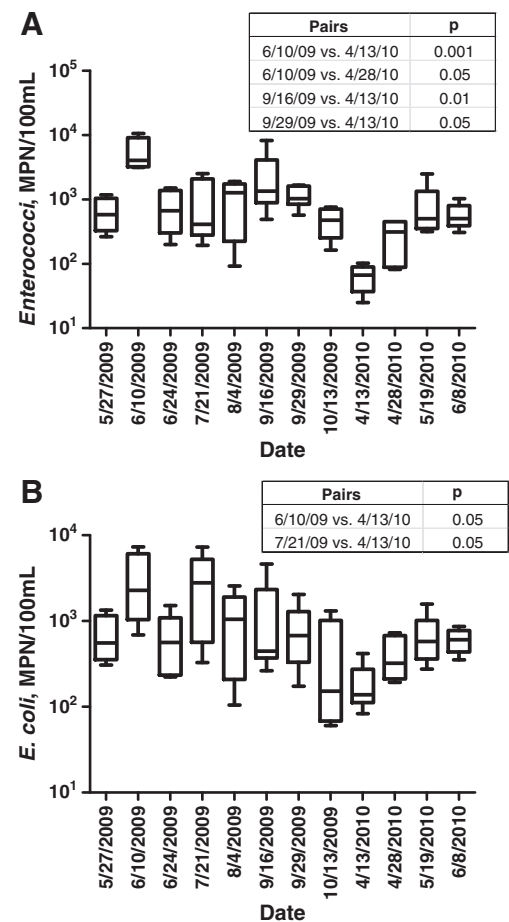

Fig. 5. Temporal (A) and spatial analysis (B) of arsenic. Whiskers represent minimum and maximum values, the box encloses the interquartile range, and the line within the box represents the median. Significant differences in the median concentrations for paired sites are listed. No significant differences in the median concentrations between paired dates were observed.

Fig. 6. Temporal analysis of bacteria in the water column: A — *Enterococci* and B — *E. coli*; spatial analysis of bacteria in the water column: C — *Enterococci* and D — *E. coli*; temporal analysis of bacteria in the sediment: E — *Enterococci* and F — *E. coli*; spatial analysis of bacteria in the sediment: G — *Enterococci* and H — *E. coli*. Whiskers represent minimum and maximum values, the box encloses the interquartile range, and the line within the box represents the median. Significant differences in the median concentrations for paired dates are listed. No significant differences in the median concentrations between paired sites were observed.

(Fig. 6C, D). Changes in bacterial counts in the sediment level were mostly not significant from either a spatial (land use) or temporal perspective (Fig. 6E–H).

3.5. Effects of land use on analytes

The relationships between percent land use and the mean concentrations of ortho-P, PP, arsenic, and nitrate-N were examined. Ortho-P and nitrate-N were not correlated with either forest or agricultural land use ($0.01 \leq R^2 \leq 0.15$). Somewhat surprisingly, a strong negative correlation was observed between PP and agricultural land use ($R^2 = 0.80$, $p = 0.02$) and strong positive correlation to forest lands ($R^2 = 0.92$, $p = 0.002$). Similarly, a strong, negative correlation was observed between arsenic and forest lands ($R^2 = 0.85$, $p = 0.008$), whereas, only a weak-negative, and not significant, correlation between arsenic and agriculture (cropland area) was found ($R^2 = 0.32$, $p = 0.2$). These results can be explained by considering the catchment areas where both arsenic and PP concentrations were largest: 1, 3, and 6. These three catchments are headwaters and contain a substantial amount of forest in addition to cropland. In contrast, low arsenic and PP concentrations were observed in catchment area 2 which has a lower forested area and receives little overland flow from AFOs. In catchment area 5, land use is mostly agricultural and receives little AFO drainage.

Finally, the effect of catchment size on mean concentration was examined. Ortho-P was positively correlated ($R^2 = 0.5$; $p = 0.1$) and PP was negatively correlated ($R^2 = 0.4$; $p = 0.2$,) to catchment size. Although neither correlation was significant, these correlations may reflect the fortuitous positive correlation of size to residential area ($R^2 = 0.97$; $p = 0.0003$) and that the smaller catchments 1, 3, and 6 receive waters from the poultry houses. No correlation was observed for the other analytes.

4. Conclusions

This study was conducted to examine in greater resolution the effects of land use and characteristics on the water quality parameters of a subwatershed in the Choptank River watershed. The catchments within the subwatershed were defined using advanced remotely-sensed data and current geographic information system processing techniques (Lang et al., 2012). However, service roadways at some poultry production facilities were found to redirect runoff from the facilities to neighboring catchment areas. These altered overland flow pathways affected water quality parameters. Catchments with larger residential areas were also shown to affect the nutrient profile observed in water samples.

Climatic conditions and land use metrics are frequently used to predict water quality, but this study demonstrated that analysis of land use and hydrological pathways for each catchment may need greater detail to avoid erroneous conclusions. *Enterococci* and *E. coli* concentrations were ubiquitous in this subwatershed and showed no correlation to location or land use, although some dependence upon precipitation was observed. Nitrate-N concentration values are usually associated with the amount of agricultural land use or with large urban sources. As this subwatershed is 68% agriculture and 11% residential, and the apparent lack of correlation between nitrate-N and agriculture may reflect the small change in percent agriculture and/or the similarity of agronomic practices and crops produced among the catchments of this subwatershed. Agronomic practices and climate conditions appeared to affect ammonia emission and deposition to water surfaces especially in the local area. The negative correlation of PP and arsenic with percent forest was unexpected, yet this effect was explained by the stronger signal of the head waters and overland flow versus groundwater inputs.

Although this survey was conducted over a period of just over one year, temporal trends were not found; however, some significant spatial differences in analyte concentrations were observed. Poultry production facilities in this subwatershed generally exhibited higher arsenic and PP concentration values, compared to other catchment areas where no poultry houses were present. This arsenic signal in the catchments, however, is muted at best when examined at the larger watershed scale (Whitall et al., 2010). Historical use of lead arsenate used in apple production did occur throughout this region and may be a potential source of arsenic. However, this signal would most likely be observed in all catchments and not necessarily correlated to poultry production. Finally, the arsenic link to poultry production may become a less effective indicator because in June 2011 the manufacturer of roxarsone agreed to remove all arsenic-containing feed additives from animal feed due to the potential human toxicity risk associated with consuming poultry produced with this feed additive (Erickson, 2011). Thus, a new search for a unique set of AFO indicators will be needed.

Nomenclature

AFO	animal feeding operation
ARS	Agricultural Research Service
BFI$_{max}$	Maximum Baseflow Index
CASTNET	Clean Air Status and Trends Network
CEAP	Conservation Effects Assessment Project
DEM	Digital Elevation Model
GC	gas chromatography
HPLC	high performance liquid chromatography
LOQ	limit of quantitation
LiDAR	light detection and ranging
MCL	maximum contaminant level
NOAA	National Oceanic and Atmospheric Administration
PP	particle phase phosphorus
TMDL	total maximum daily load
TP	total phosphorus
US	United States
USDA	United States Department of Agriculture
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey

Disclaimer

Mention of specific products is for identification and does not imply endorsement by the US Government to the exclusion of other suitable products or suppliers.

Acknowledgments

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